

Tetraphenylarsonium Chloride as an Analytical Reagent

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

By
George McClellan Smith
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For the frequent advice, constant interest and patient supervision of Professor H. H. Willard, under whose direction this investigation has been conducted, the author expresses his sincere appreciation.

Tetraphenylarsonium Chloride as an Analytical Reagent

Titration by Iodine

HOBART H. WILLARD AND GEORGE M. SMITH,¹

University of Michigan, Ann Arbor, Mich.

METHODS in which tetraphenylarsonium chloride may be used as an analytical reagent for mercury, tin, cadmium, zinc, and perhenate have been developed by the authors and will be described in subsequent papers. Lamprey

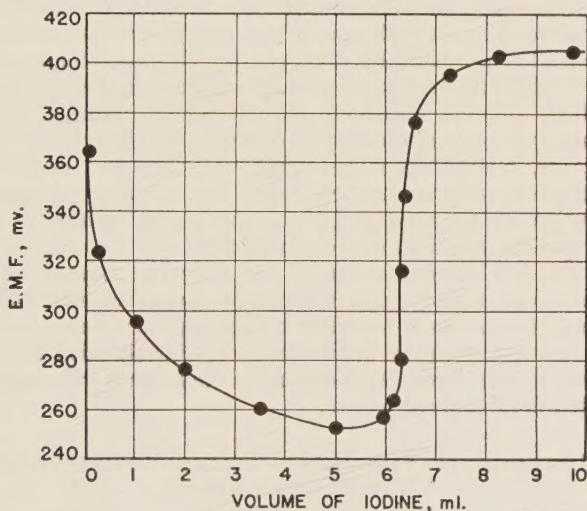


FIGURE 1. TETRAPHENYLARSONIUM CHLORIDE TITRATED WITH IODINE

Solution saturated with sodium chloride

(3), who did the exploratory research in connection with the reagent, showed that it could be used for the determination of perchlorate, periodate, gold, and platinum, but his studies were not exhaustive. He showed that the reagent could be used gravimetrically, or volumetrically by titrating the excess of standard reagent potentiometrically with iodine.

Tetraphenylarsonium chloride (obtainable from Merck & Co.) was prepared according to the method of Blicke and Marzano (1), with slight modifications developed by the

¹ Present address, Vanderbilt University, Nashville, Tenn.

authors and others. According to Blicke and Monroe (2) the aqueous solution is a strong electrolyte which yields tetraphenylarsonium, $(C_6H_5)_4As^+$, and chloride ions.

Three types of reactions have been noted in which the reagent is serviceable:

1. The formation of insoluble salts by the combination of the tetraphenylarsonium ion with such ions as perrhenate, permanganate, periodate, and perchlorate. Such determinations were most conveniently made gravimetrically.

2. The formation of insoluble compounds by the combination of the tetraphenylarsonium ion and the complex mercuric, stannic, cadmium, and zinc chloride ions. Such determinations were made by titrating the excess of standard tetraphenylarsonium chloride potentiometrically with iodine.

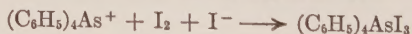
3. The formation of insoluble compounds with such thiocyanate complexes as those of iron and cobalt. These reactions have not yet been thoroughly investigated, but they appear to present analytical possibilities.

The analytical behavior of several other arsonium ions was studied. Although all gave precipitates resembling those obtained with tetraphenylarsonium ion, none reacted quantitatively with iodine or with perchlorate, perrhenate, or chlorocadmiate ions. The compounds were similar to tetraphenylarsonium chloride with one of the phenyl groups replaced by an alkyl or substituted alkyl group. The compounds tried were iodomethyltriphenylarsonium chloride, triphenylarsinehydroxy chloride, phenacyltriphenylarsonium chloride, allyltriphenylarsonium bromide, β -hydroxyethyltriphenylarsonium chloride, methyltriphenylarsonium chloride, and carboxymethyltriphenylarsonium chloride. The effect of the substitution of an alkyl group for the phenyl group is to increase the solubility of the compounds.

Since the determinations of the mercuric, stannic, cadmium, and zinc ions depend upon the potentiometric titration of the excess of standard tetraphenylarsonium chloride by means of standard iodine solution, this titration is discussed in this paper. Applications of the reagent will be presented in subsequent papers.

Potentiometric Titration of Tetraphenylarsonium Chloride with Iodine

This titration, by means of which the tetraphenylarsonium chloride solution is standardized, depends upon the reaction



and the fact that there is a sudden large increase in the oxidation potential when an equivalent quantity of iodine containing iodide has been added to the tetraphenylarsonium chloride solution (Figure 1). It is seen from the equation that one molecular weight of tetraphenylarsonium chloride requires two atomic weights of iodine and one of iodide.

The reaction is carried out in volumes less than 150 ml. in saturated sodium chloride solution. Since the product, a rusty-orange precipitate, does not form unless the iodine

solution contains potassium iodide, it is evident that the reaction consists of the union of the tetraphenylarsonium and periodide ions rather than the union of tetraphenylarsonium chloride and iodine, as had originally been supposed. This is indicated by the data of Table I, secured by weighing the precipitates obtained from several potentiometric titrations. Measured volumes of standard tetraphenylarsonium chloride solution were titrated potentiometrically with standard iodine solution. The precipitates were filtered through Gooch crucibles, washed with water, dried at 105° C., and weighed. Within the limits of experimental error the observed weights of the precipitates are the same as the weights of tetraphenylarsonium periodide calculated from the volume of standard

TABLE I. GRAVIMETRIC DETERMINATION OF TETRAPHENYLARSONIUM ION

[5 ml. of $(C_6H_5)_4AsCl$ in 100 ml. of saturated NaCl solution]		
I_2 Used	$(C_6H_5)_4AsI_3$ Calcd.	$(C_6H_5)_4AsI_3$ Found
Mg.	Mg.	Mg.
13.83	41.6	41.8
13.83	41.6	41.6
13.80	41.5	41.7
13.87	41.7	41.8
13.83	41.6	41.6

iodine used. However, the gravimetric standardization of the reagent with excess iodine is not as convenient nor as precise as the potentiometric method.

The potentiometric standardization is carried out as follows:

Five to 10 ml. of the aqueous tetraphenylarsonium solution, 0.01 to 0.03 *M*, are measured and diluted to nearly 100 ml. with water or saturated sodium chloride solution. The reference and

TABLE II. EFFECT OF SODIUM CHLORIDE CONCENTRATION ON TITRATION

[1 ml. of reagent solution contains 4.086 mg. of $(C_6H_5)_4AsCl$]		
NaCl	$(C_6H_5)_4AsCl$	$(C_6H_5)_4AsCl$
Moles/l.	Ml.	Mg./ml.
0	20	4.10
0	10	4.12
0	5	4.18
0	1	4.39
1.00	5	4.14
2.50	5	4.11
4.00	5	4.084
4.50	5	4.090
5.00	20	4.080
5.00	10	4.080
5.00	5	4.082
5.00	2	4.087

indicator electrodes are immersed in this solution while standard iodine solution of about the same concentration, containing 6 to 8 grams of potassium iodide per liter, is added slowly with constant stirring. As the iodine is added the potential of the system steadily decreases to a minimum value. When this minimum is reached, the iodine is added dropwise and time allowed for the system to reach equilibrium. When an equivalent quantity of iodine has been added there is a sudden increase in potential amounting to 25 to 35 millivolts per 0.01 ml. of 0.02 *N* iodine. Near the end point the solution must be completely saturated with salt before the titration is completed.

Any type of potentiometer system may be used. The indicator electrode was a smooth platinum wire and the reference electrode a calomel half-cell.

By the above procedure 4 to 100 mg. of tetraphenylarsonium chloride can be determined conveniently, and successive titrations duplicated within 0.02 to 0.03 ml. of 0.02 *N* iodine solution. The optimum concentration is 10 to 50 mg. of the reagent in about 100 ml. of solution, although acceptable results are obtained in 200 ml. It is best to saturate with sodium chloride just before the end point is reached. The time required is 20 to 30 minutes.

For best results the temperature of the solution being titrated should be 20° to 30° C., and never above 40° to 45° C., because of the volatility of the iodine and the increased solubility of the periodide precipitate.

TABLE III. SOLUBILITY OF TETRAPHENYLARSONIUM CHLORIDE IN AQUEOUS SODIUM CHLORIDE SOLUTIONS

(60-Ml. volume. Temperature, 30° C.)		
NaCl	(C ₆ H ₅) ₄ AsCl	(C ₆ H ₅) ₄ AsCl
Moles/l.	G./100 ml.	Mole/l.
0	32.50	0.776
1.0	10.43	0.240
2.0	1.27	0.038
2.5	0.459	0.011
3.0	0.205	0.0049
3.5	0.101	0.0024
4.5	0.034	0.00081
Satd.	0.011	0.00026

The influence of the sodium chloride concentration is shown by Table II. Equilibrium is attained very slowly in low salt concentrations, thus making the titration very slow and uncertain. However, when the solution is almost saturated

TABLE IV. SOLUBILITIES OF TETRAPHENYLARSONIUM HALIDES

Compound	(Temperature, 25° C.)	
	Solubility G./100 ml.	Mole/l.
Tetraphenylarsonium fluoride	17.45	0.434
Tetraphenylarsonium chloride (30° C.)	32.50	0.776
Tetraphenylarsonium bromide	1.29	0.0279
Tetraphenylarsonium iodide	0.14	0.0028

with sodium chloride, equilibrium is reached in a short time, and constant and easily reproducible results are obtained. A small amount of potassium iodide produces similar results but may form insoluble tetraphenylarsonium iodide.

Although the tetraphenylarsonium chloride precipitates slowly, it is insoluble in concentrated sodium chloride solution, as Table III shows. Since the conversion of solid tetraphenylarsonium chloride to the periodide is very slow, it is best to avoid formation of the solid by beginning the titration with a moderate salt concentration and completing the saturation just before the end point is reached. The standard iodine solution should not contain more than 6 to 8 grams of potassium iodide per liter of 0.01 to 0.02 *N* solution; otherwise insoluble tetraphenylarsonium iodide will form.

The solubilities in water of other tetraphenylarsonium halides at 25° C. were investigated, and are presented in Table IV.

A typical titration curve is shown in Figure 1. The first portion of the curve, in which the potential falls rather sharply as the iodine is added, probably corresponds to the removal of tetraphenylarsonium ion. The potential rises abruptly with the first slight excess of iodine, and the addition of a further excess causes a negligible change.

The direct titration of the reagent with iodine, or the titration of the excess of iodine with standard thiosulfate in the presence of the periodide precipitate with starch as the indicator, is impossible, since the color of the precipitate obscures the color of the starch-iodide complex. The potentiometric titration of excess iodine with thiosulfate in the presence of the precipitate is impossible because of the uncertainty of the end point.

TABLE V. EFFECT OF ACIDITY AND NITRATES ON TITRATION

[5 ml. of $(C_6H_5)_4AsCl$ in 100 ml. of solution saturated with salt]

Iodine Required Ml.	Substances Present besides Sodium Chloride
4.58	None
4.58	Concd. HCl, 2.0 ml.
4.56	Concd. HCl, 3.0 ml.
4.57	$NaNO_3$ (neutral), 2.0 grams
4.58	$NaNO_3$, 2.0 grams
	Concd. HCl, 0.2 ml.
4.58	$NaNO_3$ (neutral), 10.0 grams
	80% salt satn.
4.50	$NaNO_3$, 10.0 grams
	Concd. HCl, 1.0 ml.
	80% salt satn.
4.35	$NaNO_3$, 10.0 grams
	Concd. HCl, 1.0 ml.
	80% salt satn.
	More time allowed than in preceding titration

The presence of free acid, except nitric acid, in moderate amounts is not objectionable, as shown by Table V. Nitric acid, and nitrates in the presence of acid, oxidize the iodide in the standard iodine solution to free iodine, causing the end point to be premature. When nitrates are present, the solution is neutralized to methyl red with sodium bicarbonate before titrating. Large quantities of nitrate cause the precipitation of tetraphenylarsonium nitrate.

Other chlorides, except those capable of oxidizing iodide or reducing iodine and those that form complex halide ions, may be substituted for sodium chloride. Other salts, such as sulfates, are not as effective in coagulating the precipitate. The alkalis and alkaline earths, nickel, cobalt (ous), chromium, manganese, borate, bicarbonate, acetate, phosphate, sulfate, citrate, and tartrate even in fairly high concentration do not interfere. The solution must be neutral or slightly acid. All anions that form fairly insoluble compounds with the reagent—e. g., tungstate, molybdate, chromate, perhenate, permanganate, periodate, perchlorate, iodide (except in the iodine solution), bromide and fluoride—and all cations that form complex halide ions—e. g., zinc, cadmium, mercuric,

thallic, stannic, bismuth, ferric, platinum, and auric—interfere.

Ferrous ion (100 mg. or less) may be present. When ferric ion is present the addition of about 2 ml. of sirupy phosphoric acid and 2 grams of disodium phosphate will eliminate interference up to 200 mg. of iron, but results are not ideal with

TABLE VI. EFFECT OF CERTAIN CATIONS ON TITRATION

[5 ml. of $(C_6H_5)_4AsCl$ in 100 ml. of solution saturated with sodium chloride.
5 ml. of $(C_6H_5)_4AsCl$ are equivalent to 7.17 ml. of iodine solution]

Iodine Required Ml.	Substances Present besides Sodium Chloride
7.18	$MnCl_2 \cdot 2H_2O$, 1 gram
7.17	$CrCl_3 \cdot 6H_2O$, 1 gram
7.17	Sodium citrate, 8.8 grams
7.23	Sodium citrate, 17.5 grams
7.17	Cu^{++} , 400 mg.
	Sodium citrate, 4 grams
7.16	Cd^{++} , 88 mg.
	Sodium citrate, 4.5 grams
7.20	Zn^{++} , 10 mg.
	Sodium citrate, 4.5 grams
7.28	Bi^{+++} , 33 mg.
	Sodium citrate, 4.5 grams
7.33	Sn^{++++} , 16 mg.
	Sodium citrate, 4.5 grams
7.16	Fe^{+++} , 200 mg.
	Disodium phosphate, 2 grams
7.22	$FeSO_4 \cdot 7H_2O$, 500 mg.

amounts beyond 100 mg. Citrate and tartrate are not effective in this respect, but citrate prevents interference by rather large amounts of cupric ion and by very small amounts (a very few milligrams) of tin, bismuth, zinc, and cadmium. A few grams of sodium citrate and enough citric acid to make the solution acid to methyl red are added before titrating. Table VI shows the effect of various cations on the titration.

All common organic solvents interfere either by preventing precipitation or by obscuring the end point.

Summary

Tetraphenylarsonium chloride is useful as a reagent for determining mercuric, stannic, cadmium, zinc, perrhenate, periodate, perchlorate, and other ions.

Periodate, perchlorate, permanganate, perrhenate, fluoride, bromide, iodide, thiocyanate, molybdate, chromate, tungstate, and large amounts of nitrate interfere by forming insoluble salts with the reagent.

Mercury, tin, cadmium, zinc, platinum, gold, bismuth, and iron, the complex halide ions of which form insoluble compounds with the reagent, and all ions that can oxidize iodide or reduce iodine interfere.

Interference by copper, iron, cadmium, zinc, bismuth, and tin may be eliminated to some extent.

The reagent may be standardized potentiometrically with standard iodine, the reaction producing a rusty-orange precipitate of tetraphenylarsonium periodide.

The total volume to be titrated should be about 100 ml. of neutral or slightly acid solution saturated with sodium chloride just before the end point is reached.

Literature Cited

- (1) Blicke and Marzano, *J. Am. Chem. Soc.*, **55**, 3056 (1933).
- (2) Blicke and Monroe, *Ibid.*, **57**, 720 (1935).
- (3) Lamprey, H., thesis, University of Michigan, 1935.

FROM a thesis presented by G. M. Smith to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of doctor of philosophy.

Tetraphenylarsonium Chloride as an Analytical Reagent

Determination of Mercury, Tin, Cadmium, and Zinc

HOBART H. WILLARD and GEORGE M. SMITH,¹

University of Michigan, Ann Arbor, Mich.

Mercuric ion (0.5 to 100 mg.) can be quantitatively precipitated as $[(C_6H_5)_4As]_2HgCl_4$ by tetraphenylarsonium ion in a 1.0 to 2.5 *M* sodium chloride solution in a volume of 30 to 120 ml. The determination cannot be made gravimetrically, but only by titrating potentiometrically the excess of reagent with iodine. Free acid, 0.2 to 1.0 *M*, except nitric acid, does not interfere. The precipitate does not form in alkaline solution. MnO_4^- , ReO_4^- , ClO_4^- , IO_4^- , I^- , Br^- , F^- , WO_4^{--} , MoO_4^{--} , CrO_4^{--} , CNS^- , Bi^{+++} , Pt^{++++} , Sn^{++++} , Zn^{++} , Cd^{++} , Ti^{+++} , and those ions that react with iodide ion or with iodine interfere. Interference by Cu^{++} , Sn^{++++} , Mn^{++} , Fe^{+++} , and Ti^{++++} may be eliminated by the formation of certain stable complex ions.

Tin (0.80 to 84.0 mg.) in a volume of 30 to 120 ml. can be determined quantitatively by precipitation as $[(C_6H_5)_4As]_2SnCl_6$ with an excess of standard tetraphenylarsonium chloride and the subsequent potentiometric titration of the excess with iodine, or by the direct potentiometric titration of the dissolved precipitate. The precipitate should be formed in a solution 0.4 to 2.0 *M* in hydrochloric acid and 1.5 to 3.0 *M* in sodium chloride, depending upon the quantity of precipitate, and allowed to stand 30 to 60 minutes before filtering. Fe^{+++} , more than 25 mg. of Fe^{++} , Pt^{++++} , Au^{+++} , Bi^{+++} , Hg^{++} , Cd^{++} , Zn^{++} , Ti^{+++} , Sb^{+++} , As^{+++} , UO_2^{++} , F^- , $C_2O_4^{--}$, PO_4^{--} , acetates, citrates, alkaline substances and all anions precipitated by the reagent must be absent.

Cadmium and zinc may be quantitatively determined by precipitation with an excess of tetraphenylarsonium chloride in 3.0 to 3.5 *M* sodium chloride solution, and the subsequent potentiometric

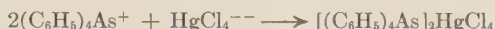
¹ Present address, Vanderbilt University, Nashville, Tenn.

metric titration of the excess with iodine. The precipitates are somewhat more soluble than those of mercury and tin formed under similar conditions. In addition to those ions which interfere in the determination of tin, interference by manganese, cobalt, copper, and iron is more serious here. Interference by small amounts of tin may be avoided by the addition of tartrate.

THE potentiometric titration of tetraphenylarsonium chloride with iodine, upon which determinations of mercury, stannic, cadmium, and zinc ions depend, has been discussed in a previous paper (2).

Determination of Mercury

In the presence of an excess of chloride ion the mercuric ion forms the complex halide ion, HgCl_4^{--} . The determination of mercury with tetraphenylarsonium ion depends upon the reaction



The compound is white and crystalline, insoluble in sodium chloride solution, but fairly soluble in water.

A gravimetric determination was not feasible, since no suitable wash liquid could be found. The tetraphenylarsonium compounds of the mercuric complexes of the other halogens behave similarly, but are not suitable for analytical work since tetraphenylarsonium bromide and iodide are precipitated also.

Although a gravimetric determination is impossible, mercury can be determined by precipitating the compound with an excess of standard reagent in sodium chloride solution and, after filtering the precipitate, titrating the excess of reagent potentiometrically with iodine, in the manner already described (2). The method is rapid and accurate. A direct potentiometric titration between the mercuric and tetraphenylarsonium ions was found to be impossible. Lamprey (1) reported a conductometric determination based on this reaction but showed no data in support.

For this work standard solutions of tetraphenylarsonium chloride, mercuric ion, and iodine were required. The 0.01 to 0.03 *N* iodine solution, standardized by means of arsenite, contained 6 to 8 grams of potassium iodide per liter. The 0.01 to 0.03 *M* tetraphenylarsonium chloride solution was made by dissolving 5 to 10 grams of reagent per liter and standardizing it potentiometrically with standard iodine (2). The mercuric solution was made by dissolving 5.1106 grams of pure mercury in 50 ml. of 50 per cent nitric acid. The solution was boiled to remove nitrous fumes, the excess nitric acid was neutralized with sodium hydroxide, and the solution was diluted to 1000 ml. after being slightly acidified with hydrochloric acid.

PROCEDURE. The solution of mercuric ion, prepared as described, is diluted to about 30 ml. and enough commercial (non-iodized) sodium chloride is added to form a 1.0 to 2.5 *M* solution after the addition of the tetraphenylarsonium chloride. Standard 0.01 to 0.02 *M* reagent, in not more than 10-ml. excess, is added during constant stirring. The volume should now be 60 to 120 ml., depending upon the quantity of mercury present. The precipitate is allowed to stand 15 to 60 minutes and filtered through a Gooch crucible. The precipitate is washed several times with saturated sodium chloride solution, and the filtrate and washings are titrated potentiometrically with standard iodine as already described.

This titration determines the excess of standard tetraphenylarsonium chloride used and, by difference, the volume of reagent required to remove the mercury quantitatively. The quantity of mercury present is determined by this volume of reagent and is calculated from the standardization of iodine with arsenious oxide, the volume of tetraphenylarsonium chloride equivalent to 1 ml. of standard iodine, and the equation given above. One milliliter of 0.01 *M* tetraphenylarsonium chloride is equivalent to 1.0031 mg. of mercury.

The error involved in determining quantities of mercury from 0.5 to 107 mg. in pure solutions is about ± 0.06 mg.

TABLE I. EFFECT OF VARIOUS ANIONS

(Mercury present, 25.64 mg.; volume, 60 ml.; 7.85 ml. excess reagent)	NaCl, <i>M</i>	Addition Agent Salt	<i>M</i>	Mercury Found	Mercury Error
				<i>Mg.</i>	<i>Mg.</i>
2.3		NaNO ₃	0.7	25.77	+0.13
2.3		(NH ₄) ₂ SO ₄	1.0	25.66	+0.02
2.3		NaOAc	1.0	25.68	+0.04
2.3		NaHCO ₃	3.0	25.67	+0.03
1.1		Na ₂ HPO ₄	0.5	25.61	-0.03
1.1		Na ₂ B ₄ O ₇	0.1	25.64	0.00
1.1		K ₂ C ₄ H ₄ O ₆	0.1	25.62	-0.02
1.1		Na ₃ C ₆ H ₅ O ₇	0.2	25.69	+0.05
1.1		NaNO ₃	0.1	...	...
		Na ₂ SO ₄	1.0	25.80	+0.16
1.1		NaNO ₃	1.0	...	...
		Na ₂ SO ₄	0.2	25.68	+0.04
2.3		NaNO ₃	0.1	...	...
		Na ₂ SO ₄	0.1	...	...
		NaOAc	4.0	25.76	+0.12
		<i>Gram</i>			
1.1		H ₂ SeO ₃	1.0	25.71	+0.07
1.1		K ₂ TeO ₃	1.0 TeO ₂	25.72	+0.08

For the larger quantities, 1.1 *M* and for the smaller, 2.5 *M* sodium chloride are most suitable. If the precipitate is small a considerable excess of reagent and several hours' standing are desirable. The presence of solid tetraphenylarsonium chloride is shown by the appearance of long needlelike crystals.

The most important factors studied were (1) the most suitable sodium chloride concentration, (2) the most suitable excess of reagent, (3) the proper volume for precipitation, (4) the time the precipitate should stand before being filtered, (5) the limits of the efficiency of the method, and (6) the influence of the presence of other substances.

EFFECT OF SODIUM CHLORIDE CONCENTRATION. The most satisfactory concentrations are between 1.0 *M* and 2.5 *M*.

In these concentrations the precipitate is composed of much larger crystals and is therefore more easily transferred. Precipitation is incomplete in lower concentrations. In higher concentrations tetraphenylarsonium chloride may precipitate with the chloromercuriate compound, if a considerable excess is present.

EFFECT OF VARYING EXCESS OF TETRAPHENYLARSONIUM CHLORIDE. Since the solubility of tetraphenylarsonium chloride decreases greatly with increased sodium chloride concentration (2), a greater excess may be used if the chloride concentration is fairly low. The permissible excess also is less with the higher concentrations of mercury. Therefore, if the quantity of mercury is large, requiring a large volume of reagent, the sodium chloride concentration should be about 1.0 *M* for best results. Since tetraphenylarsonium chloride is almost quantitatively insoluble in 3.0 *M* sodium chloride, the permissible excess of reagent under these conditions is very low, and the precipitate must be filtered almost immediately. From 2 to 15 ml. of 0.01 to 0.02 *M* tetraphenylarsonium chloride may be used in excess in salt concentrations between 1.0 and 2.5 *M*. Since it is impossible to tell when an excess of reagent has been added, a preliminary determination should be made to determine the approximate quantity of mercury.

EFFECT OF VOLUME. The total volume in which the precipitation is made should be kept as low as possible, so that the filtrate and washings will not exceed 100 ml., in order to secure the best conditions for titrating the excess of reagent with standard iodine. Satisfactory results were obtained, however, in volumes varying from 30 to 200 ml. Only the larger quantities of mercury were precipitated in volumes greater than 100 ml. The precipitate is somewhat more crystalline in the larger volumes. For practical purposes, depending upon the quantity of mercury, the volume was 60 to 120 ml. If there was less than 5 mg. of mercury the volume was still smaller.

If the solution is heated the precipitate is more crystalline, but filtrations must always be made at room temperatures.

EFFECT OF TIME OF STANDING. For a moderate excess of reagent the time seems of no considerable importance. In general, if the quantity of precipitate is large filtration should take place soon after the solutions are thoroughly mixed. If the amount of precipitate is small 15 to 60 minutes should elapse.

EFFECT OF ACIDITY. The precipitate is somewhat soluble in acid of high concentration. Therefore the mercury solution must be neutralized with sodium bicarbonate or sodium hydroxide, then sufficient hydrochloric acid added to make the solution 1 *M*, after which the sodium chloride and reagent are added. In 1 *M* hydrochloric acid better results are secured with 2.3 *M* sodium chloride. Higher acid concentrations retard precipitation. Nitric and sulfuric acids behave in the same way, but all free nitric acid must be removed before the filtrate is titrated with iodine. The organic acids interfere more seriously than others, but, in general, 0.2 *M* acids of any

kind are not detrimental to the process. Free alkalis and ammonia prevent precipitation.

INTERFERING SUBSTANCES. Most of the common anions, except nitrate in rather high concentration, do not interfere. Nitrate causes the precipitation of tetraphenylarsonium nitrate. Those anions which react with tetraphenylarsonium ion— MnO_4^- , CrO_4^{--} , WO_4^{--} , MoO_4^{--} , IO_4^- , ClO_4^- , ReO_4^- , I^- , Br^- , F^- , and CNS^- —and those that react with iodine or with iodide ion must be absent.

Cations that form halide complexes, and consequently precipitate with tetraphenylarsonium ion— Bi^{+++} , Sn^{++++} , Pt^{++++} , Au^{+++} , Tl^{+++} , Zn^{++} , Cd^{++} , and Fe^{+++} —and those that oxidize iodide ion or reduce iodine must be absent. The addition of certain substances to form stable complex ions may permit the presence of certain of these interfering cations, as Table II shows. High concentrations of manganese interfere. Ferrous ion interferes with the titration of the excess reagent unless the end point is known approximately and quickly reached. The influence of certain cations is shown in Table II.

TABLE II. EFFECT OF VARIOUS METALLIC IONS

(Mercury present, 25.64 mg.; 60-ml. volume; 7.85 ml. excess reagent)

NaCl, M	Addition Agent Salt	M	Mercury Found	Mercury Error
			Mg.	Mg.
2.3	$\text{Mg}(\text{OAc})_2$	1.0	25.58	-0.06
None	AlCl_3	1.1	25.73	+0.09
None	BaCl_2	1.1	25.67	+0.03
None	CaCl_2	1.1	25.67	+0.03
1.1	CoSO_4	0.25	25.67	+0.03
1.1	CrCl_3	1 g.	25.60	-0.04
1.1	FeSO_4	0.5	25.64	0.00
None	MnCl_2	0.6	25.81	+0.17
1.1	MnCl_2	0.1	25.71	+0.07
None	NH_4Cl	2.3	25.60	-0.04
1.1	PbCl_2	0.5	25.67	+0.03
1.1	NiSO_4	0.25	25.66	+0.02
1.1	$\text{UO}_2(\text{OAc})_2$	0.1	25.73	+0.09
1.1	ZrOCl_2	0.05	25.56	-0.08

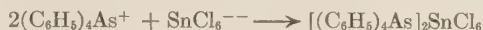
Cupric ion does not interfere with the precipitation of the mercury compound, but interferes with the titration of the filtrate by oxidizing iodide ion to iodine. This interference may be avoided, as Table III shows, by adding sodium citrate and citric acid before titrating. Tartrate is not effective with copper, but is effective, if added before precipitation, in eliminating interference by manganese and stannic ions, for which citrate is not effective. Titanium, in the form of the double oxalate, does not interfere.

Interference by ferric ion is best avoided by adding, before precipitating the mercury compound, about 0.5 ml. of sirupy phosphoric acid per 100 mg. of ferric ion, or until the yellow color is removed. After the removal of the mercury precipitate, the quantity of acid is doubled and an equal weight of disodium phosphate added. Thereupon the titration is carried out as usual. This treatment is effective for as much as 300 mg. of ferric ion. Fluoride cannot be used for this purpose because of the slight solubility of a tetraphenylar-

sonium compound. Interference by more than traces of cadmium, zinc, and bismuth cannot be eliminated.

Determination of Tin

In slightly acid solution, containing an excess of chloride ion, quadrivalent tin is precipitated completely by tetraphenylarsonium ion. The precipitated tetraphenylarsonium chlorostannate, $[(C_6H_5)_4As]_2SnCl_6$, is white, crystalline, soluble in water and alkalis, but insoluble in concentrated chloride solutions. The precipitation is due to the reaction



and in very weakly acid solutions is incomplete and somewhat colloidal.

As in the case of mercury, the determination cannot be made gravimetrically since no suitable wash liquid has been found. Neither can it be determined by a direct potentiometric titration between the two ions, although it is possible to determine the tin by titrating the dissolved precipitate potentiometrically with iodine. The most practical method, however, is the same as that for the determination of mercury—precipitation of the tin with an excess of standard tetraphenylarsonium chloride and potentiometric titration of the filtered excess with standard iodine.

TABLE III. ELIMINATION OF INTERFERENCE BY CERTAIN IONS
(Mercury present, 25.64 mg.; 60-ml. volume; NaCl 1.1 to 2.3 M)

Ion Present	Addition Agent		Mercury Found	Mercury Error
	Mg.		Mg.	Mg.
Cu ⁺⁺	400	Sodium citrate, 3 grams Citric acid to acidify	25.67	+0.03
Mn ⁺⁺	1900	Potassium tartrate, 4.7 grams	25.74	+0.10
Sn ⁺⁺⁺⁺	32	Potassium tartrate and tartaric acid	25.65	+0.01
Ti ⁺⁺⁺⁺	90	Sodium oxalate and HCl	25.69	+0.05
Fe ⁺⁺⁺	21	Disodium phosphate, 2 grams H ₃ PO ₄ , 2 ml.	25.67	+0.03
Fe ⁺⁺⁺	103	Disodium phosphate, 2 grams H ₃ PO ₄ , 2 ml.	25.64	0.00
Fe ⁺⁺⁺	206	Disodium phosphate, 2 grams H ₃ PO ₄ , 2 ml.	25.69	+0.05
Fe ⁺⁺⁺	309	Disodium phosphate, 3 grams H ₃ PO ₄ , 2 ml.	25.69	+0.05
Fe ⁺⁺⁺	515	Disodium phosphate, 3 grams H ₃ PO ₄ , 2 ml.	Unsatisfactory	

The titration indicates by difference the volume of reagent required to precipitate the tin. From the equation it is seen that 1 ml. of 0.01 M tetraphenylarsonium chloride is equivalent to 0.5935 mg. of tin.

Three standard solutions were required in this investigation—0.02 to 0.03 N iodine, 0.01 to 0.02 M tetraphenylarsonium chloride, and a standard tin solution. The first two solutions were made in the manner already described (2). The tin solution was made by dissolving 1.9705 grams of pure tin in concentrated hydrochloric acid while a slow stream of chlorine was passed through the gently boiling solution.

When the metal was dissolved completely the excess of chlorine was expelled by a current of air, and the solution was cooled and diluted to 500 ml. Thus, each milliliter contained 3.941 mg. of tin and a small amount of acid.

PROCEDURE. To the tin solution, in as small volume as possible, 2 ml. of concentrated hydrochloric acid and enough commercial noniodized sodium chloride are added to give a 2.5 to 3.0 *M* concentration of sodium chloride in a final volume of 60 ml. A measured volume of standard tetraphenylarsonium chloride, known to be in excess, and enough water to give a volume of 60 ml. are added during constant stirring. If additional tetraphenylarsonium chloride is needed to complete the precipitation no additional salt need be added, but the acid concentration should always be 0.4 to 1.0 *M*. The concentration of sodium chloride should be 2.5 to 3.0 *M* for quantities of tin up to 30 mg. and may drop to 1.5 to 2.0 *M* for larger quantities.

When the precipitate has settled completely and has stood 30 to 60 minutes, it is filtered through a Gooch crucible and washed several times with saturated sodium chloride. The combined filtrate and washings are titrated potentiometrically with standard iodine (2) to determine the excess of reagent. If there is a large quantity of precipitate it is not necessary that it stand so long before filtering.

The factors studied in this determination are the same as those studied in the determination of mercury.

EFFECT OF SODIUM CHLORIDE CONCENTRATION. The concentration required for quantitative precipitation of the tin compound is higher than that required in the determination of mercury. Good results were obtained with sodium chloride concentrations between 2.5 and 3.5 *M*. With high concentrations only a very small excess of reagent may be used and the precipitate must be filtered very quickly to avoid precipitating some of the reagent. For large quantities of tin, the sodium chloride concentration need not be greater than 2.0 *M*.

INFLUENCE OF ACIDITY. Unless the mixture has a certain minimum acidity the precipitate is somewhat colloidal, probably because of hydrolysis. To secure good results the solution should be at least 0.4 *M* with hydrochloric acid, and the concentration may be as high as 2.0 *M*. There is no precipitation in alkaline or neutral solutions.

Since the sodium chloride concentration is higher than in the mercury determination, the maximum excess of reagent must be less. The excess should never be greater than 10 ml. of 0.015 *M* reagent, preferably less in 2.5 to 3.0 *M* sodium chloride, to avoid precipitating the reagent.

The mixture must be well stirred and the precipitate permitted to settle completely. This should require not less than 15 minutes nor more than 60 minutes for average quantities of tin. If the precipitate is bulky, as in the case of quantities of tin greater than 50 mg., this time may be shortened. For very small precipitates more time may be required. For average amounts, good results were obtained by filtering after 45 minutes.

As in the case of mercury, the least possible volumes were used for best results—from 30 to 120 ml., depending upon the

quantity of tin present. Most determinations were carried out in a volume of 60 ml.

Heating the mixture offers no advantage other than to cause the precipitate to form more slowly and in larger crystals. The filtration should never be made at temperatures higher than room temperature.

Three to 8 ml. of excess reagent were used in all the determinations. A series of results not recorded here showed that 0.80 to 84.0 mg. of tin was determined with an error of ± 0.06 mg. A 3- to 8-ml. excess of reagent was used in all cases. The determination of quantities larger than 84 mg. of tin is hindered by the bulkiness of the precipitate, making it

TABLE IV. EFFECT OF CERTAIN ANIONS

(20.98 mg. of Sn; 2.5 *M* NaCl; 60-ml. volume; constant-volume reagent. Concentrated acids used in every case)

Added Substances	Tin Found Mg.	Tin Error Mg.
HCl, 2 ml.	20.98	0.00
HNO ₃ , 2 ml.	20.99	+0.01
NaNO ₃ , 4 grams	21.03	+0.05
HCl, 2 ml.		
H ₂ SO ₄ , 2 ml.	21.06	+0.08
H ₂ SO ₄ , 5 ml.	20.96	-0.02
Na ₂ SO ₄ ·10H ₂ O, 5 grams	20.95	-0.03
HCl, 2 ml.		
Acetic acid, 2 ml.	20.96	-0.02
Acetic acid, 5 ml.	20.71	-0.27
Acetic acid, 5 ml.	20.90	-0.08
HCl, 2 ml.		
Sodium acetate, 4 grams	No precipitate	
HCl, 2 ml.		
H ₃ BO ₃ , 0.7 gram	20.97	-0.01
Tartaric acid, 2 grams	20.49	-0.49
Tartaric acid, 2 grams	20.95	-0.03
HCl, 2 ml.		
Potassium tartrate, 2 grams	20.89	-0.09
HCl, 2 ml.		
Citric acid, 4 grams	No precipitate	
HCl, 2 ml.		
H ₃ PO ₄ , 2 ml.	10.61	-10.37
Na ₂ HPO ₄ ·12H ₂ O, 4 grams	No precipitate	
HCl, 2 ml.		
Na ₂ C ₂ O ₄ , 1 gram	Precipitation incomplete	
HCl, 2 ml.		
NH ₄ F, 1 gram	Precipitation incomplete	
HCl, 2 ml.		

difficult to filter and wash, and increasing the probability of adsorbing some of the reagent.

INTERFERING SUBSTANCES. Substances that interfere with the determination of tin by tetraphenylarsonium ion fall generally into three classes: (1) those that prevent the complete precipitation of the tin compound, (2) those that are precipitated by the reagent, and (3) those that interfere with the iodine titration. To the first class belong all those substances which react with tin to form complexes, such as phosphate, citrate, oxalate, and fluoride, and those that render the solution alkaline or neutral, such as sodium hydroxide, sodium bicarbonate, and neutral buffers. To the second class belong such anions and cations as perhenate, permanganate, periodate, perchlorate, iodide, bromide, fluoride, tungstate, chromate, thiocyanate, platinum, ferric, bismuth, thallic, mercuric, cadmium, zinc, and auric. In the third class are those that reduce iodine or oxidize iodide ion, such as stannous, antimony, nitrate, cupric, and ferric.

It is necessary that all substances of the three classes, except cupric and nitrate ions, be absent in these determinations. Interference by cupric ion may be avoided by adding sodium citrate and citric acid, as with mercury, but the addition must not be made until the tin precipitate has been removed. All free nitric acid must be neutralized before the potentiometric titration.

Organic acids and phosphoric acid interfere. The presence of hydrochloric acid with acetic or tartaric acid largely eliminates this interference, but has no effect with acetates, citric acid or citrates, phosphates, oxalates, or fluorides.

Table V shows the effect of certain cations. No way could be found to avoid interference by ferric ion since stannic and ferric ions form similar complexes. Ferrous ion apparently does not interfere with the precipitation of the tin compound, but satisfactory end points could not be obtained in the titrations when more than 25 to 35 mg. of ferrous ion were present. Uranyl ion interferes.

TABLE V. EFFECT OF CERTAIN CATIONS

(20.98 mg. of Sn; 2.5 *M* NaCl; 0.4 *N* HCl; 25 ml. of 0.015 *M* reagent; volume, 60 ml.)

Added Substances	Tin Found <i>Mg.</i>	Tin Error <i>Mg.</i>
Al ⁺⁺⁺ , 0.3 gram	20.99	+0.01
BaCl ₂ , 2.5 <i>N</i> (no NaCl)	20.94	-0.04
BaCl ₂ , 1.2 <i>N</i> (1.5 <i>N</i> NaCl)	20.99	+0.01
CaCl ₂ , 2.5 <i>N</i> (no NaCl)	21.00	+0.02
Co ⁺⁺ , 0.45 gram	20.99	+0.01
Cr ⁺⁺⁺ , 0.39 gram	20.94	-0.04
Cu ⁺⁺ , 0.4 gram	21.01	+0.03
Mg ⁺⁺ , 0.3 gram	20.99	+0.01
Mn ⁺⁺ , 0.55 gram	21.00	+0.02
NH ₄ Cl, 2.5 <i>M</i> (no NaCl)	20.92	-0.06
NH ₄ Cl, 1.2 <i>M</i> (2.0 <i>M</i> NaCl)	20.94	-0.04
Ni ⁺⁺ , 0.42 gram	20.98	0.00
Pb ⁺⁺ , 0.55 gram	20.86	-0.12
H ₂ SO ₄ , 2 ml. (no HCl)		
Th ⁺⁺⁺⁺ , 0.66 gram	20.99	+0.01
UO ₂ ⁺⁺ , 0.64 gram	No excess reagent left	
Zr ⁺⁺⁺⁺ , 0.4 gram	20.94	-0.04

It was found that the tin could be determined by titrating the tetraphenylarsonium ion in the precipitate. The precipitate, after being filtered and washed as usual, was dissolved in hot water and the titration made potentiometrically with standard iodine (2). The solution was allowed to cool to room temperature before the end point was reached and was not saturated with sodium chloride until that time, to avoid precipitating the tin compound again. Considerable time was required to effect complete solution, but the addition of a few milliliters of ammonium hydroxide aids this process. When solution is complete this solution is made neutral or very slightly acidic.

The accuracy is almost equal to that of the parallel indirect determination, as Table VI shows, but the latter method is to be preferred in general because of the time required to effect solution, and the much larger volume of iodine required for the direct titration. This large quantity of iodine forms a very bulky periodide precipitate which reduces the sensitivity

of the reaction near the end point. The method might be employed profitably for less than 10 mg. of tin.

Determination of Cadmium and Zinc

Cadmium and zinc may be determined with tetraphenylarsonium chloride by procedures similar to those for mercury and tin. In highly concentrated chloride solutions the complex chloride ions of cadmium, CdCl_4^{--} , and zinc, ZnCl_4^{--} , form insoluble white crystalline precipitates of tetraphenylarsonium chlorocadmiate, $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{CdCl}_4$, and tetraphenylarsonium chlorozincate, $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{ZnCl}_4$, respectively. The precipitation is quantitative in the proper sodium chloride concentration if a sufficient excess of reagent is used, but the compounds are soluble in water. The chlorocadmiate precipitate is slightly more soluble than the corresponding chlorostannate precipitate and considerably more soluble than the chloromercuriate compound. This is indicated by the sodium chloride concentration required to cause complete precipitation. The chlorozincate compound is even more soluble. Because of this rather high solubility the deter-

TABLE VI. DETERMINATION OF TIN BY DIRECT TITRATION OF PRECIPITATE

Indirect Titration	Direct Titration	Error
Mg.	Mg.	Mg.
7.80	7.73	-0.07
19.19	19.12	-0.07
19.50	19.55	+0.05
19.57	19.63	+0.06
19.62	19.64	+0.02
19.64	19.72	+0.08
19.74	19.83	+0.09

minations are, in general, subject to more interferences than the others.

The determinations were carried out, as usual, by titrating the excess of tetraphenylarsonium ion potentiometrically with iodine, using 0.015 to 0.020 *M* tetraphenylarsonium chloride and titrating with 0.020 to 0.025 *N* iodine solution containing 6 to 10 grams of potassium iodide per liter. The calculations of the quantities of cadmium or zinc are made in the usual way. One milliliter of 0.01 *M* tetraphenylarsonium chloride is equivalent to 0.5621 and 0.3269 mg. of cadmium and zinc, respectively. Solutions made from pure metallic cadmium and zinc were used in this work.

Since rather high sodium chloride concentrations (2.5 to 3.5 *M*) must be used, a limited excess of tetraphenylarsonium chloride must be used because of its slight solubility in high chloride concentrations. The permissible excess may be somewhat larger in highly acid solutions. Attempts to find an indicator for an excess of reagent were unsuccessful. Therefore it is necessary to run a trial determination to determine the approximate quantity of metal present.

On account of the solubility of these precipitates in water it seems certain that they could be dissolved and titrated di-

TABLE VII. EFFECT OF VARIOUS IONS ON DETERMINATION OF CADMIUM

(Volume, 60 ml.; HCl, 0.3 *M*. Precipitates stood one hour. Cadmium present, 23.00 mg.; theoretical excess of reagent, 8.72 ml.)

NaCl, <i>M</i> ₀	Substances Present	Cadmium Error
3.0	NH ₄ NO ₃ , 1 gram	<i>M</i> ₀ .
3.2	NH ₄ NO ₃ , 1 gram	+0.10
3.2	NH ₄ NO ₃ , 0.5 gram	+0.19
3.0	K ₂ SO ₄ , 5 grams	-0.02
3.2	K ₂ SO ₄ , 1 gram	+2.07
3.0	Borax, 1 gram	-0.01
3.3	Borax, 1 gram	+0.04
3.3	Disodium phosphate, 1 gram	+0.01
3.3	Sodium acetate, 1 gram	-0.05
3.3	Sodium formate, 1 gram	+0.03
3.3	Ammonium tartrate, 1 gram	+0.25
3.3	Sodium citrate, 1 gram	+0.07
None	Ammonium chloride, 3.3 <i>M</i>	+0.08
None	Ammonium chloride, 3.7 <i>M</i>	+0.23
None	Potassium chloride, 3.7 <i>M</i>	-0.07
None	Calcium chloride, 3.3 <i>M</i>	-0.03
None	Barium chloride, 1.7 <i>M</i>	-0.08
2.8	Ni ⁺⁺ , 223 mg.	+0.03
3.0	Mg ⁺⁺ , 120 mg.	+0.10
3.0	Al ⁺⁺⁺ , 150 mg.	+0.05
3.0	Co ⁺⁺ , 248 mg.	+0.09
3.0	Co ⁺⁺ , 248 mg.	+0.75
	Ammonium tartrate, 2 grams	+0.11
2.8	Ni ⁺⁺ , 223 mg.	+0.06
	Ammonium tartrate, 2 grams	
2.8	Cr ⁺⁺⁺ , 100 mg.	+0.07
3.0	Cr ⁺⁺⁺ , 255 mg.	+3.07
3.0	Cu ⁺⁺ , 255 mg.	+0.09
	Sodium citrate, 2 grams	
2.8	Mn ⁺⁺ , 277 mg.	+0.70
2.8	Mn ⁺⁺ , 277 mg.	+0.04
	Ammonium tartrate, 4 grams	
3.0	Fe ⁺⁺⁺ , 103 mg.	+0.76
	Sodium phosphate, 2 grams	
	Phosphoric acid, 2 ml.	
2.7	Fe ⁺⁺⁺ , 103 mg.	+0.23
	Sodium phosphate, 2 grams	
	Phosphoric acid, 2 ml.	
2.0	Fe ⁺⁺⁺ , 103 mg.	+0.12
	Sodium phosphate, 2 grams	
2.5	Pb ⁺⁺ , 273 mg.	-0.06
	H ₂ SO ₄ , 3 ml.	
2.7	Sn ⁺⁺⁺⁺ , 22.5 mg.	-0.05
	Ammonium tartrate, 2 grams	
3.0	Sn ⁺⁺⁺⁺ , 45 mg.	+0.04
	Ammonium tartrate, 2 grams	

TABLE VIII. EFFECT OF VARIOUS IONS ON DETERMINATION OF ZINC

Volume, 60 ml.; HCl, 0.3 *M*; precipitates stood 1 to 2 hours. Zinc, 15.40 mg.; theoretical excess of reagent, 9.70 ml., 0.015 *M*)

NaCl, <i>M</i>	Substances Present	Zinc Error <i>Mg.</i>
3.0	NH ₄ NO ₃ , 1 gram	-0.07
3.0	K ₂ SO ₄ , 1 gram	-0.07
3.2	Borax, 1 gram	-0.04
3.0	Sodium phosphate, 1 gram	+0.03
3.5	Sodium acetate, 1 gram	+0.06
3.0	Sodium formate, 1 gram	-0.04
3.0	Sodium citrate, 1 gram	-0.07
2.7	Sodium citrate, 4 grams	+0.19
	Citric acid, 2 grams	
3.3	Ammonium tartrate, 1 gram	-0.03
3.0	Ammonium tartrate, 1 gram	-0.09
None	Ammonium chloride, 3.7 <i>M</i>	-0.05
None	Potassium chloride, 3.5 <i>M</i>	+0.01
None	Calcium chloride, 1.8 <i>M</i>	-0.06
None	Barium chloride, 1.5 <i>M</i>	-0.04
3.0	Ni ⁺⁺ , 223 mg.	-0.11
2.8	Ni ⁺⁺ , 223 mg.	+0.05
	Ammonium tartrate, 2 grams	
3.0	Mg ⁺⁺ , 120 mg.	-0.08
3.0	Al ⁺⁺⁺ , 150 mg.	+0.03
3.2	Cr ⁺⁺⁺ , 100 mg.	-0.01
2.8	Co ⁺⁺ , 124 mg.	+0.04
2.8	Co ⁺⁺ , 248 mg.	+0.55
2.8	Co ⁺⁺ , 248 mg.	+0.06
	Ammonium tartrate, 2 grams	
2.8	Co ⁺⁺ , 248 mg.	+0.04
	Sodium citrate, 3 grams	
2.8	Cu ⁺⁺ , 128 mg.	-0.08
2.8	Cu ⁺⁺ , 255 mg.	+1.89
2.8	Cu ⁺⁺ , 255 mg.	+0.15
	Sodium citrate, 3 grams	
2.8	Mn ⁺⁺ , 277 mg.	+0.40
2.8	Mn ⁺⁺ , 277 mg.	+0.40
	Ammonium tartrate, 4 grams	
2.8	Mn ⁺⁺ , 277 mg.	-0.07
	Sodium acetate, 4 grams	
2.8	Mn ⁺⁺ , 277 mg.	+0.07
	Sodium phosphate, 4 grams	
2.5	Fe ⁺⁺⁺ , 103 mg.	+0.15
	Sodium phosphate, 4 grams	
2.8	H ₂ PO ₄ , 1.5 ml.	+0.09
2.8	Pb ⁺⁺ , 273 mg.	+0.09
2.8	H ₂ SO ₄ , 3 ml.	-0.03
	Sn ⁺⁺⁺ , 45 mg.	
	Ammonium tartrate, 2 grams	

rectly with iodine, as in the case of tin, although this was not done.

PROCEDURE FOR DETERMINATION OF CADMIUM. The acidity of the cadmium solution, in as small volume as possible, is so adjusted that the hydrochloric acid concentration will be about 0.3 *N* in a final volume of 60 ml. Sufficient commercial (non-iodized) sodium chloride is added to make a 3.0 to 3.5 *M* solution. An excess of standard tetraphenylarsonium chloride solution is added, and the mixture is diluted to 60 ml., stirred vigorously, and allowed to stand about an hour before filtering through a Gooch crucible. The lower concentration of sodium chloride is best, and it may be reduced to 2.5 *M* if the concentration of other salts is high. The excess of reagent in 3.0 *M* sodium chloride solution should not exceed that amount which can remain dissolved in this volume—i.e., about 9 to 10 ml. of 0.015 *M* reagent in 3.0 *M* sodium chloride solution.

The precipitate is filtered and washed with a saturated sodium chloride solution. The solution and washings are titrated potentiometrically with standard iodine in the usual way, to obtain by difference the volume of reagent required to precipitate the cadmium.

A series of determinations showed that quantities of cadmium varying from 0.4 to 65 mg. in pure solutions could be determined with an error of ± 0.09 mg. but the excess of reagent was more critical than in the case of mercury and tin. It appeared probable that larger amounts could be determined.

The best sodium chloride concentration is 3.0 to 3.5 *M*. At lower concentrations precipitation is incomplete, and at higher concentrations the reagent is likely to contaminate the precipitate.

The best results are obtained in solutions with acidity varying from faintly acid to 0.4 *M* in hydrochloric acid. Nitric acid precipitates tetraphenylarsonium nitrate and also interferes with the subsequent titration. Organic acids interfere in some cases by forming complexes with the cadmium which hinder precipitation.

INTERFERING SUBSTANCES. Cadmium is subject to the same interferences as mercury and tin. Because of the higher concentrations of sodium chloride and the ability of cadmium to form complexes with certain organic acids, some ions interfere that do not interfere with mercury or even with tin. These include cupric, cobaltous, manganous, and ferric ions. It is possible to avoid interference by these ions when they are present in smaller quantities than those shown in the cases of mercury and tin.

Those ions that form rather stable chloride complexes, such as mercuric, stannic, auric, platinic, zinc, ferric, cupric, cobaltous, and manganous ions interfere, as do such anions as the halides (other than chloride), thiocyanate, perchlorate, periodate, perrhenate, permanganate, nitrate, and those ions that are capable of oxidizing or reducing the iodine solution.

Table VII shows the effect of the presence of certain ions and how certain interferences may be avoided.

The phosphates and tartrates yield copious precipitates

with the above metals and cause some of the tetraphenylarsonium to be salted out if the solution stands too long. In the case of cupric ion the citrate and acid must be added before the precipitation is made. Interference by small amounts of stannic ion may be avoided by the addition of tartrate ion.

PROCEDURE FOR DETERMINATION OF ZINC. The procedure is identical with that for cadmium, except that the sodium chloride concentration should be nearer 3.5 *M* than 3.0 *M* for best results. Fairly satisfactory results may be obtained in 3.0 *M* sodium chloride if the maximum excess of reagent is used and the mixture allowed to stand about 3 hours before filtering.

Although solid tetraphenylarsonium chloride precipitates rather slowly in 3.0 to 3.5 *M* sodium chloride solutions, it is best to use no larger excess than can remain in solution in the aqueous sodium chloride—i. e., about 9 ml. of 0.015 *M* reagent in 3.5 *M* sodium chloride. With 4.0 *M* sodium chloride good results are obtained, but the excess of reagent is rather critical. With more than 45 mg. of zinc the precipitate becomes inconveniently bulky, and with less than 0.3 mg. the solubility error is too great and the time required is too long. The error in a series of experiments on pure solutions was ± 0.09 mg.

The acid concentration supplied only by hydrochloric acid should not be greater than 0.4 *M*. If the solution is made about 0.3 *M* a slightly larger excess of reagent may be used safely and the precipitate allowed to stand longer before filtering. No zinc precipitates in alkaline solution.

INTERFERING SUBSTANCES. Zinc is subject to the same interferences as cadmium. These interferences may be aggravated somewhat by the higher sodium chloride concentration required to effect complete precipitation of the zinc complex. The means whereby, and the extent to which, interference may be avoided are the same as for cadmium. If the concentration of other substances is unusually high the concentration of sodium chloride should be reduced to 2.5 to 3.0 *M* to avoid salting out the excess tetraphenylarsonium chloride. Interference by mercury and cadmium cannot be avoided to any extent, although interference by as much as 50 mg. of stannic ion may be eliminated by the addition of 2 to 4 grams of an alkali tartrate. Interference by manganese may be avoided by use of acetate, phosphate, or tartrate. (Table VIII.)

Literature Cited

- (1) Lamprey, H., thesis, University of Michigan, 1935.
- (2) Willard and Smith, *IND. ENG. CHEM., Anal. Ed.*, **11**, 186 (1939).

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